NAREL Standard Operating Procedure
For Radium-228 in Environmental Matrices

Effective July 21, 2011

AM/SOP-13

National Air and Radiation Environmental Laboratory
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1.0 PURPOSE

1.1 This document describes a method used for measuring the concentration of ^{228}Ra in environmental samples.

1.2 The method can be applied to samples being analyzed only for ^{228}Ra, or to a sequential analysis for ^{228}Ra following preparation and analysis for ^{226}Ra.

2.0 SCOPE AND APPLICATION

2.1 This method is used to measure the concentration of ^{228}Ra in environmental samples including water, soil, sediment, and vegetation.

2.2 Solid samples requiring analysis for radium are prepared using *NAREL Standard Operating Procedure for Preparing Solid Samples for Radium-226 and Radium-228 Analysis* (AMS/SOP-1).

2.3 Water samples requiring analysis for radium are prepared using *NAREL Standard Operating Procedure for Preparing Water Samples for Radium-226 and Radium-228 Analysis* (AMS/SOP-2).

2.4 The detection and quantification capabilities of this method are functions of sample size, interferences, chemical recovery of the isotopes, instrument efficiency and background, and counting time. The actual MDA and reporting limit for each sample may be different based on any of these variables. For clean water samples, using a 1 L aliquant, a minimum detectable activity (MDA) of 1 pCi/L for ^{228}Ra is obtainable. For soil samples, using a 0.5 g aliquant, a minimum detectable activity (MDA) of 2 pCi/g for ^{228}Ra is obtainable.

2.5 Radium is precipitated as a radium-barium sulfate. The precipitate is dissolved in a pentasodium diethylenetriamine pentaacetate (Na_5DTPA) solution. Radium-228 is a weak beta emitter and the ^{228}Ac daughter is allowed to grow in for 36 h. The ^{228}Ac is then extracted with di-2-ethylhexylphosphoric acid (HDEHP) and back-extracted with nitric acid. The ^{228}Ac is beta-counted in a low-background proportional counter.

2.6 Interferences

2.6.1 There are no known interferences with this method.

2.7 There is no isotope of actinium available to monitor the chemical recovery of ^{228}Ac. The chemical recovery is obtained from a standard sample spiked with ^{228}Ra. The unknown sample and the standard sample must be analyzed exactly alike for this method to work properly.

3.0 DEFINITIONS

3.1 **CERLS –** Center for Environmental Radioanalytical Laboratory Science, formerly the Monitoring and Analytical Services Branch (MASB) – the Center at NAREL responsible for analyzing samples for radioactive constituents and hazardous chemicals.

3.2 **CAS Registry No (CASRN) –** Chemical Abstract Service Registry Number.

3.3 **control chart** - a graph for monitoring the outputs of a process, such as an analytical measurement process, for the purpose of detecting conditions or trends adverse to quality.

3.4 **laboratory control sample (LCS)** - an artificial sample generated by the analyst in the laboratory and spiked with a known amount of one or more analytes. After being spiked,

the LCS is prepared and analyzed in the same manner as a normal sample, and the result of the measurement is compared to the known amount of analyte added to assess the bias of the measurement process.

3.5 **LIMS** – Laboratory Information Management System – a database and software system used to manage radioanalytical data, monitor work processes, and produce reports.

3.6 **matrix spike (MS)** - an artificial sample generated by the analyst in the laboratory. An aliquant is taken from one sample at the same time another aliquant is taken for normal preparation and analysis. The second aliquant is spiked with a known amount of one or more analytes. After being spiked, the MS is prepared and analyzed in the same manner as a normal sample, and the result of the measurement is compared to the unspiked aliquant to assess the effect of the matrix on the performance of the analytical method.

3.7 **method blank** – an artificial sample generated by the analyst in the laboratory, which is as free as possible of the analyte of interest. The method blank is prepared and analyzed in the same manner as a normal sample and alongside real samples, so that the result of the measurement may be used to assess low-level bias in the measurement process, such as that caused by contamination of reagents, as well as cross-contamination of samples.

3.8 **MSDS –** acronym for material safety data sheet, a document that contains information on the potential health effects of exposure to chemicals or other potentially dangerous substances, and on safe working procedures workers should adhere to when handling chemical products.

3.9 **NAREL** – National Air and Radiation Environmental Laboratory.

3.10 **NIST –** acronym for National Institute of Standards and Technology, formerly the National Bureau of Standards (NBS), which is the national standards body for the United States and a member organization of the International Organization for Standardization (ISO).

3.11 **QAM** – QA Manager – Quality Assurance Manager – person with primary responsibility for overseeing NAREL's quality system.

3.12 **R value** – the ratio of observed activity divided by the actual amount of added activity, a measure of recovery.

3.13 **replicate sample (duplicate)** – an aliquant taken from one sample at the same time another aliquant is taken for normal preparation and analysis. Both aliquants are prepared and analyzed in the same manner. The analytical result for the second aliquant is compared to the result of the first aliquant to assess the precision of the measurement process.

3.14 **SHEM** – Safety, Health and Environmental Manager – person with primary responsibility for overseeing NAREL's Health and Safety Program.

3.15 **SOP –** acronym for standard operating procedure, a document that describes in detail the steps for performing a routine task.

4.0 EQUIPMENT AND SUPPLIES

4.1 Centrifuge.

4.2 Planchet, stainless steel, 5 cm diameter.

4.3 Separatory funnel, 125 mL, 250 mL and 2000 mL.

4.4 Magnetic stirrer and stir bar.

4.5 Suction filter apparatus, Kontes filter funnel, 2000 mL filter flask.

4.6 Assorted glassware.

4.7 pH meter.

4.8 40 mL centrifuge tube.

4.9 Hot plate.

4.10 Desiccator.

4.11 Analytical balance.

4.12 Top-loading balance.

4.13 Beakers,100 mL.

5.0 REAGENTS AND STANDARDS

5.1 Acetic acid (CH_3COOH), glacial, 17 M (CAS: 64-19-7). Reagent grade.

5.2 Acetic acid (CH_3COOH), 6 M. Dilute 345 mL of the 17 M CH_3COOH to 1 L with demineralized water.

5.3 Chloroacetic acid ($CH_2ClCOOH$) (CAS: 79-11-8).

5.4 Diethylenetriamine pentaacetic acid, pentasodium salt (Na_5DTPA) (CAS: 140-01-2). Reagent grade.

5.5 Sodium hydroxide (NaOH) (CAS: 1310-73-2).

5.6 Actinium wash solution. Dissolve 100 g $CH_2ClCOOH$ and 2.4 mL of Na_5DTPA in 800 mL of demineralized water, adjust the pH to 3.0 with NaOH using a pH meter, and dilute to 1 L with demineralized water.

5.7 Ammonium hydroxide (NH_4OH) 15 M (CAS: 1336-21-6). Reagent grade.

5.8 Chloroacetic acid ($CH_2ClCOOH$) 2 M. Add 189 g of $CH_2ClCOOH$ to a beaker. Dissolve in 800 mL of demineralized water and dilute to 1 L with demineralized water.

5.9 Diammonium citrate [$(NH_4)_2HC_6H_5O_7$] (CAS: 3012-65-5).

5.10 Diammonium citrate [$(NH_4)_2HC_6H_5O_7$] 2 M. Dissolve 226.2 g of $(NH_4)_2HC_6H_5O_7$ in demineralized water and dilute to 500 mL with demineralized water.

5.11 Di-2-ethylhexylphosphoric acid (HDEHP) (CAS: 298-07-7).

5.12 n-Heptane [$CH_3(CH_2)_5CH_3$] (CAS: 142-82-5). Reagent grade.

5.13 Di-2-ethylhexylphosphoric acid wash solution (HDEHP wash solution). Mix 100 mL of 2 M $(NH_4)_2HC_6H_5O_7$ and 100 mL of 15 M NH_4OH. NOTE: The HDEHP wash solution should be prepared on the same day that it is used. The solution complexes after sitting for more than 24 h, causing emulsions to form during the extractions.

5.14 Di-2-ethylhexylphosphoric acid (HDEHP) 15 % in n-heptane. Dilute 150 mL HDEHP to 1 L with n-heptane and transfer to a 2 L separatory funnel. Wash the HDEHP twice with 100 mL aliquots of the HDEHP wash solution. Shake the funnel for 1 min, venting frequently. Allow the layers to separate and discard the lower layer. Wash the HDEHP twice with 100 mL aliquots of 4 M HNO_3. Shake the funnel for 1 min, venting frequently. Allow the layers to separate and discard the lower layer. Store the cleaned HDEHP solution in a polyethylene bottle.

5.15 Perchloric acid ($HClO_4$) 12 M (CAS: 7601-90-3). Reagent grade.

5.16 Diethylenetriamine pentaacetic acid, pentasodium salt (Na_5DTPA), 0.17 M, pH 10. Add 209 mL of Na_5DTPA to 400 mL of demineralized water and filter through 2.4 cm glass fiber filter with suction. Adjust to pH 10 using a pH meter. Use $HClO_4$ to lower the pH or NaOH to raise the pH. Dilute to 1 L with demineralized water and store in a polyethylene bottle.

5.17 Hydrochloric acid (HCl) 12 M (CAS: 7647-01-0). Reagent grade

5.18 Hydrochloric acid (HCl) 4 M. Dilute 333 mL of 12 M HCl to 1 L with demineralized water.

5.19 Nitric acid (HNO_3) 16 M (CAS: 7697-37-2). Reagent grade.

5.20 Nitric acid (HNO_3) 4 M. Dilute 250 mL of 16 M HNO_3 to 1 L with demineralized water.

5.21 Nitric acid (HNO_3) 1 M. Dilute 63 mL of 16 M HNO_3 to 1 L with demineralized water.

5.22 Sodium sulfate (Na_2SO_4), anhydrous (CAS: 7757-82-6).

5.23 Sodium sulfate (Na_2SO_4), 20 %. Dissolve 20 g Na_2SO_4 in 70 mL demineralized water and dilute to 100 mL.

5.24 Sulfuric acid (H_2SO_4), 18 M (CAS: 7664-93-9). Reagent grade.

5.25 Acetone (CH_3COCH_3) (CAS: 67-64-1). Reagent grade.

5.26 NIST-traceable standard solution containing about 1500 – 5000 dpm/mL of ^{89}Sr.

5.27 Silica gel desiccant (CAS: 63231-67-4).

5.28 Ethyl alcohol (C_2H_5OH) (CAS: 64-17-5).

6.0 SAFETY

6.1 All procedures performed at NAREL must be conducted following the requirements detailed in the *NAREL Chemical Hygiene Plan* and the *NAREL Radiation Safety Manual*. Safety precautions associated with handling of chemical reagents, solutions, and all samples are the primary responsibility of the analyst. Any spills or accidents involving hazardous, corrosive, or toxic material must be immediately resolved.

6.2 Unnecessary or prolonged exposure to laboratory chemicals should be avoided.

6.3 All NAREL laboratory personnel are expected to use good laboratory practices. Most of the safety training is provided by the SHEM officer. The analyst is expected to comply with all directives given by the SHEM officer, and must take necessary precautions to prevent exposure or injury to both self and co-workers.

6.4 Adding concentrated nitric acid to the samples containing reactive materials, opening, and venting digested sample vessel may result in the release of toxic vapors, such as nitrogen oxide fume. All work must be performed in a properly ventilated fume hood. When adding concentrated nitric acid to the sample, the analyst should also be aware of the potential for a vigorous reaction. If a vigorous reaction occurs, allow to cool before capping the vessel.

6.5 Nitric acid is poisonous, reactive, and a strong oxidizer. It can cause burns to body tissues and may be fatal if ingested or inhaled. Vapors are irritating to eyes and mucous membranes. Use only with adequate ventilation and proper protective clothing and gloves. Nitric acid is incompatible with most substances, especially strong bases, metallic powders, carbides, and combustible organics. Store away from light and heat.

6.6 Hydrochloric acid is harmful if swallowed, inhaled, or ingested. It can cause serious damage to eyes and skin. Ingestion can cause burns around the mouth, throat, and

esophagus with irritation and pain. Hydrochloric acid causes chemical burns following contact with skin and eyes. Inhalation can cause toxic effects and may be fatal. Use hydrochloric acid only with adequate ventilation and appropriate protective clothing. Always release caps slowly to ensure slow dissipation of vapors. Store concentrated hydrochloric acid in the original container, securely sealed, in a cool, dry, well-ventilated area, away from alkaline materials, galvanized steel, and zinc. Avoid strong bases.

6.7 Sodium hydroxide can produce severe chemical burns in the mouth and intestinal tract. Accidental ingestion may be cause burns, ulcerations, and swelling of the mucous membranes, and can result in respiratory distress, asphyxia, and shock. Sodium hydroxide causes severe chemical burns to the eyes and skin after contact. Inhalation can cause respiratory irritation and pain. Do not use sodium hydroxide in aluminum, galvanized, or tin-plated containers. In the presence of moisture, sodium hydroxide is corrosive to aluminum, zinc, and tin, producing highly flammable hydrogen gas. Wear appropriate protective clothing. Always add material to water, not water to material. Store in glass or plastic container, preferably in the original container, in a cool, dry, well ventilated area. Prevent by any means possible, spillage from entering drains. Do not discharge into sewer or waterways.

6.8 Ammonium hydroxide (NH_4OH) may cause chemical burns to the eyes and skin. Adsorption through the skin may be harmful. Sodium hydroxide is harmful if swallowed causing gastrointestinal tract burns, throat constriction, vomiting, convulsions and shock. Inhalation causes chemical burns to the respiratory tract. Chronic exposure may cause liver and kidney damage and blood effects. Store in a tightly closed container in a cool, dry area away from direct sunlight.

6.9 Sulfuric acid can cause serious damage to eyes and skin. The severity of injury depends on the concentration of the solution and the duration of exposure. Ingestion can cause irritation of the respiratory tract with burning pain in the nose and throat, coughing, wheezing, shortness of breath and pulmonary edema. Use sulfuric acid only with adequate ventilation and appropriate protective clothing. Always release caps slowly to ensure slow dissipation of vapors. Store sulfuric acid in the original container, securely sealed, in a cool, dry, well-ventilated area, away from alkaline materials.

6.10 Perchloric acid is a strong oxidizer. It is corrosive and hygroscopic. It may be harmful if swallowed, and causes eye and skin burns. Perchloric acid may cause severe irritation of the respiratory tract if inhaled. Do not store perchloric acid near combustible materials. Store in a cool, dry place in a tightly closed container. Use perchloric acid only in a hood that is used exclusively for perchloric acid. Keep the hood clean and do not allow buildup of dried perchloric crystals in the hood. Solid crystals may undergo spontaneous and explosive decomposition. Always wear eye, skin, and clothing protection when using perchloric acid. Perchloric acid should be used only by persons trained and familiar with appropriate safety precautions.

6.11 Acetone is highly flammable and highly volatile. It is irritating to eyes and may cause lung damage if swallowed. Inhalation of vapors may cause dizziness or suffocation. It may cause skin irritation after prolonged or repeated exposure. Use only in a well-ventilated area. Acetone should be stored in its original container in approved flame-proof areas. Keep away from heat or ignition sources. Protect containers from physical damage and check regularly for leaks.

6.12 Ethyl alcohol is flammable as a liquid and as a vapor. Inhalation may cause dizziness and irritation to the respiratory tract. Avoid skin and eye contact by using appropriate protective clothing. Use only in a well-ventilated area away from open flames and ignition sources. Store in containers approved for ethyl alcohol.

6.13 N-heptane is highly flammable. Vapors can cause dizziness or suffocation. N--heptane must be used only in a well ventilated area. It is irritating to the skin and may cause organ damage if ingested. N-heptane must be stored away from strong oxidizers to avoid ignition. Eye protection and PVC or nitrile gloves should be worn while using n-heptane. N-heptane should be used only by persons trained and familiar with appropriate safety precautions.

6.14 Di-2-ethylhexylphosphoric acid (HDEHP) can produce chemical burns to the eye following direct contact, to the mouth and stomach if ingested, and to the skin following direct contact. Vapors or mists can be extremely irritating. HDEHP is combustible and must be stored away from strong oxidizers. Wear protective clothing including PVC gloves and safety glasses with side shields when using HDEHP. Use HDEHP only in a well ventilated area. HDEHP should be used only by persons trained and familiar with appropriate safety precautions.

6.15 Material safety data sheets (MSDS) are available to all personnel involved in chemical analysis. It is the responsibility of the analyst to be familiar with chemicals used during an analysis.

6.16 Refer to the *NAREL Chemical Hygiene Plan* for verification of appropriate safety and health practices.

7.0 ROLES AND RESPONSIBILITIES

7.1 Unless otherwise noted, the radiochemist is responsible for performing all steps of this procedure. These responsibilities include grouping samples into QC batches, performing chemical separations, maintaining control charts and recording all data in an appropriate laboratory notebook.

7.2 Counting room personnel are responsible for counting and calculating results for all prepared sources, both routine samples as well as calibration sources.

7.3 The NAREL QA Manager or QA Chemist is responsible for preparing the ^{89}Sr calibration solution and calibration verification solution

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Water samples can be shipped to the laboratory and stored in either plastic or glass containers. Nitric acid should be added to the sample in the field to bring the pH to less than 2. Upon receipt of the samples, NAREL staff check the pH of each water sample for radium analysis, and adjusts the pH as necessary. No refrigeration is required.

8.2 Soil samples can be shipped to the laboratory and stored in either plastic or glass containers. No preservation or refrigeration is required.

8.3 Special handling such as refrigeration or freezing may be required for samples of other matrices such as animal tissue or vegetation.

8.4 Samples must be stored in a safe and secure environment to maintain chain of custody.

9.0 CALIBRATION AND STANDARDIZATION

9.1 The NAREL QA Manager prepares the ^{89}Sr calibration solution and a calibration verification solution by diluting two certified NIST-traceable ^{89}Sr standards from different lots gravimetrically to 1500 – 5000 dpm/mL. The diluted solutions are maintained in the NAREL QA laboratory and distributed to analysts as needed.

9.2 Prepare a solution of ^{89}Sr containing 1500–5000 dpm/mL of activity. If the concentration is not in this range, a larger or smaller amount of the solution will be needed to prepare each calibration source.

9.3 **NOTE**: Because of its short half-life, ^{228}Ac is unsuitable for use in calibration sources. Strontium-89 is substituted because its beta spectrum is similar to that of ^{228}Ac.

9.4 Prepare nine stainless steel planchets by washing and rinsing with demineralized water and ethyl alcohol.

9.5 Prepare eight calibration sources by evaporating 1 mL of the standard solution on each of the eight planchets under a heat lamp. (If necessary, adjust the volume of standard to achieve the desired total activity per source.) Continue heating the planchets until all of the acid fumes have been removed and the planchets are dry.

9.6 Prepare one calibration verification source by evaporating 1mL of the verification solution on a planchet under a heat lamp.

9.7 Count each calibration source and the verification source in each of the low-background proportional counters to be calibrated. Count long enough to obtain 15 000 counts per source per counter.

9.8 Calculate the average total activity in each calibration source during each counting period as follows:

$$A_S = c_S V_S e^{-\lambda_S t_D} \frac{1 - e^{-\lambda_S t_S}}{\lambda_S t_S} \quad (1)$$

where

A_S is the average ^{89}Sr activity during the counting period,
c_S is the activity concentration of the ^{89}Sr standard as of its reference date and time,
V_S is the volume of the ^{89}Sr standard added to the calibration source (1 mL),
λ_S is the radioactive decay constant for ^{89}Sr (9.526×10^{-6} min^{-1}),
t_D is the elapsed time from the reference date and time of the ^{89}Sr standard to the start of the counting period (min), and
t_S is the length of the counting period (min).

Note: In several equations, including Eq. 1, a factor of the form $(1 - e^{-x})/x$ appears. This factor may be calculated in different ways. It may be approximated by $e^{-x/2}$. It may also be calculated accurately and with minimal round-off error by $e^{-x/2} \frac{\sinh(x/2)}{x/2}$.

9.9 Calculate the detection efficiency for each source as follows:

$$\varepsilon = \frac{\frac{C_S}{t_S} - \frac{C_B}{t_B}}{A_S} \quad (2)$$

where

ε is the ^{89}Sr beta counting efficiency for the source,
C_S is the source gross beta count,
C_B is the beta background count,

t_S is the source count time (min),
t_B is the background count time (min), and
A_S is the average total ^{89}Sr activity of the source during the counting period (eq. 1)

9.10 After completing the measurements of all the calibration sources on all the detectors to be calibrated, analyze the entire data set using the procedure described in Appendix 18.4 to obtain the detection efficiency and associated uncertainty for each detector.

9.11 Verify the calculated efficiency of each detector by using it to determine the activity of the calibration verification source. Compare the calculated activity of the verification source to the known activity by calculating the Z score.

10.0 PROCEDURE

10.1 If the ^{228}Ra analysis is following analysis for ^{226}Ra, obtain the sample tube from the ^{226}Ra analysis procedure (*NAREL Standard Operating Procedure for Radium-226 in Environmental Matrices, AM/SOP-12*). If analyzing only for ^{228}Ra, begin with the solution in a 100 mL beaker (from *NAREL Standard Operating Procedure for Preparing Water Samples for Radium-226 and Radium-228, AMS/SOP-2*).

10.2 Add 2 mL of 18 M H_2SO_4. Heat the sample on a hot plate at low heat for 10 min. Allow the sample to settle overnight.

10.3 Carefully decant as much clear liquid as possible without losing any precipitate. Slurry the remaining liquid with the precipitate and transfer to a 40 mL centrifuge tube. Rinse the beaker with demineralized water and add the rinse to the centrifuge tube. Centrifuge for 2 min and discard the supernate.

10.4 Add 30 mL of 0.17 M DTPA to the precipitate. Place the sample in a boiling water bath and heat using a magnetic stir bar to dissolve the precipitate (dissolution may require 30 min).

10.5 Add 1 mL of 20 % Na_2SO_4, dilute to 30 mL with demineralized water, and add 4 mL of 6 M acetic acid. Heat for 5 min in a boiling water bath while stirring with a magnetic stir bar.

10.6 Transfer the sample to an ice bath, stir and cool for 5 min. Remove the stir bar, rinse with demineralized water and centrifuge.

10.7 Repeat steps 10.3 through 10.5. Record the time of the final 6 M acetic acid addition. (Steps 10.3, 10.4, and 10.5 are performed to remove all of the ^{228}Ac present. The second $BaSO_4$ precipitation with acetic acid provides an actinium-free precipitate and begins the measured ingrowth of the ^{228}Ac from the ^{228}Ra present.)

10.8 Add 30 mL of 0.17 M DTPA to the precipitate. Place the sample in a boiling water bath and heat with stirring to dissolve the precipitate.

10.9 Allow the solution to cool to room temperature. Cover the centrifuge tube and store for at least 36 h to allow for ^{228}Ac ingrowth.

10.10 After 36 h of ingrowth, place the sample in a boiling water bath, insert a magnetic stir bar, and stir until any precipitate that may have formed during the ingrowth period has dissolved.

10.11 Add 1 mL of 20 % Na_2SO_4, dilute to 30 mL with demineralized water and add 4 mL of 6 M acetic acid. Record the time of the acetic acid addition. (The precipitation of $BaSO_4$ isolates the actinium in the supernate and ends the ^{228}Ac ingrowth period.)

10.12 Heat the sample in a boiling water bath with stirring for 5 min.

10.13 Transfer the sample to an ice bath, stir and cool for 5 min. Remove the stir bar, rinse with demineralized water, centrifuge and decant the supernate into a clean 100 mL beaker containing 10 mL of 2 M chloroacetic acid.

10.14 Measure the pH of the solution to confirm that it is 3.0. (It is important that the pH of the solution containing the actinium is 3.0. If necessary, adjust the pH with additional 2 M chloroacetic acid. Actinium extracts at a pH of approximately 3.0, so the measurement should be as close as possible.)

10.15 Add 10 mL of 15 % HDEHP for each sample being analyzed to a 250 mL separatory funnel. Add an equal volume of demineralized water and shake, venting frequently, for 1 min. Allow the layers to separate and discard the bottom layer. Add one half volume of actinium wash solution to the funnel and shake for 1 min. Allow the layers to separate and discard the bottom layer.

10.16 It is important that the HDEHP be cleaned with 4 M HNO_3 and the HDEHP wash solution, as described in step 6.14 of this document prior to using.

10.17 Transfer the sample from Step 10.13 to a 125 mL separatory funnel. Add 10 mL of the cleaned and washed 15 % HDEHP. Use the last few mL of HDEHP to rinse the beaker.

10.18 Shake vigorously for 2 min with venting. Allow the layers to separate, and discard the lower (aqueous) layer.

10.19 Add 10 mL of the actinium wash solution to the funnel. Shake for 1 min, allow the layers to separate and discard the bottom layer. Repeat the wash with an additional 10 mL of actinium wash solution and discard bottom layer.

10.20 Rinse the HDEHP with 3 mL of demineralized water, and discard lower layer. Repeat the rinse with an additional 3 mL of demineralized water and discard lower layer.

10.21 Add 10 mL of 1 M HNO_3 to the funnel. Shake for 1 min, allow the layers to separate, and collect the bottom layer in a clean 40 mL centrifuge tube.

10.22 Add an additional 5 mL of 1 M HNO_3 to the funnel and repeat the back-extraction. Combine the bottom (aqueous) layers in the centrifuge tube. Discard the top (HDEHP) layer. Use acetone to rinse the HDEHP residue from the glassware. Discard HDEHP and acetone as organic waste.

10.23 In 1 mL increments, evaporate the solution on a 5 cm planchet under a heat lamp. Heat the planchet until all of the nitric acid fumes have been removed and the sample is dry. Be careful not to evaporate to dryness until all sample is consumed. Place the sample in a desiccator, and count immediately. The half-life of ^{228}Ac is 6.15 h.

10.24 Count the sample using a low-background proportional counter and calculate the ^{228}Ra concentration.

11.0 QUALITY CONTROL PROCEDURES

11.1 Reference standards used to provide standards and calibration sources must be obtained from the National Institute of Standards and Technology (NIST) or suppliers who participate in supplying NIST standards or NIST-traceable radionuclides.

11.2 For each QC batch of up to 20 samples of the same matrix, the analyst must add the following quality control samples:

11.2.1 method blank

11.2.2 laboratory control sample

11.2.3 replicate sample (duplicate)

11.2.4 matrix spike

11.2.5 standard

11.3 Analysts are required to control chart results from blanks and laboratory control samples, and to observe the control charts for indicators of possible problems in the measurement system. LIMS software allows the analyst to input data points and to view and print the control charts.

11.4 The analyst must maintain control charts of ^{228}Ra standard yields for water and other matrices. The yield for a ^{228}Ra standard analysis is considered acceptable if it falls within the chart's three-sigma control limits and unacceptable otherwise.

11.5 See the *NAREL Radiochemistry Quality Assurance Manual* for further details on corrective actions and contingencies for handling out of control data.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 To determine the chemical recovery, first calculate the following product of decay factors for the ^{228}Ra standard.

$$F = \mathrm{e}^{-\lambda_R t_P}\, \mathrm{e}^{-\lambda_A t_D}\, \frac{1-\mathrm{e}^{-\lambda_A t_S}}{\lambda_A t_S} \tag{3}$$

where

λ_R is the radioactive decay constant for ^{228}Ra (min^{-1}),
λ_A is the radioactive decay constant for ^{228}Ac (min^{-1}),
t_p is the elapsed time from standard preparation to actinium separation (min),
t_D is the elapsed time from actinium separation to start of count (min), and
t_S is the sample count time (min).

12.2 Then calculate the chemical recovery, *Y*, and its standard uncertainty as follows:

$$Y = \frac{\frac{C_S}{t_S} - \frac{C_B}{t_B}}{c_{std} V_{std} \varepsilon F} \tag{4}$$

$$u(Y) = \sqrt{\frac{\frac{C_S}{t_S^2} + \frac{C_B}{t_B^2} + \xi_B^2}{c_{std}^2 V_{std}^2 \varepsilon^2 F^2} + Y^2 \left(\frac{u^2(c_{std})}{c_{std}^2} + \frac{u^2(V_{std})}{V_{std}^2} + \frac{u^2(\varepsilon)}{\varepsilon^2} \right)} \tag{5}$$

where

Y is the chemical recovery (fraction),
$u(Y)$ is the standard uncertainty of Y,
C_S is the standard (^{228}Ac) gross count,
C_B is the beta background count,
t_S is the sample count time (min),
t_B is the background count time (min),
ξ_B is the non-Poisson uncertainty of the background correction (cpm),
c_{std} is the activity concentration of the ^{228}Ra standard as of the standard preparation date (dpm/mL),
$u(c_{std})$ is the standard uncertainty of c_{std} (dpm/mL),

V_{std} is the volume of the ^{228}Ra standard used (mL),
$u(V_{std})$ is the standard uncertainty of V_{std} (mL),
ε is the calibrated beta detection efficiency (cpm/dpm),
$u(\varepsilon)$ is the standard uncertainty of ε, and
F is the product of decay factors for ^{228}Ra and ^{228}Ac.

12.3 Calculate the correction factor for ingrowth and decay of ^{228}Ac as follows:

$$D = \frac{\lambda_A}{\lambda_A - \lambda_R}(e^{-\lambda_R t_I} - e^{-\lambda_A t_I})e^{-\lambda_A t_D}\frac{1 - e^{-\lambda_A t_S}}{\lambda_A t_S} \quad (6)$$

where

λ_R is the decay constant for ^{228}Ra,
λ_A is the decay constant for ^{228}Ac,
t_I is the elapsed time from the radium separation to the actinium separation (min),
t_D is the elapsed time from the actinium separation to the start of the count (min), and
t_S is the sample count time (min).

12.4 Calculate the activity concentration of ^{228}Ra and its standard uncertainty as follows:

$$x = \frac{\frac{C_S}{t_S} - \frac{C_B}{t_B}}{2.22 \times V \varepsilon Y D} \quad (7)$$

$$u(x) = \sqrt{\frac{\frac{C_S}{t_S^2} + \frac{C_B}{t_B^2} + \xi_B^2}{2.22^2 V^2 \varepsilon^2 Y^2 D^2} + x^2\left(\frac{u^2(V)}{V^2} + \frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(Y)}{Y^2} + \varphi_S^2\right)} \quad (8)$$

where

x is the ^{228}Ra activity concentration (pCi/L or pCi/g),
$u(x)$ is the combined standard uncertainty of x (pCi/L or pCi/g),
D is the correction factor for ingrowth and decay of ^{228}Ac, and
C_S is the sample gross beta count,
C_B is the beta background count,
t_S is the sample count time (min),
t_B is the background count time (min),
ξ_B is the non-Poisson uncertainty of the background correction (cpm),
t_D is the time from separation to start of count (min),
V is the sample aliquant volume (L) or mass (g),
$u(V)$ is the standard uncertainty of V (L or g),
ε is the ^{228}Ac beta detection efficiency (dpm/cpm),
$u(\varepsilon)$ is the standard uncertainty of ε,
Y is the chemical recovery,
$u(Y)$ is the standard uncertainty of Y, and
φ_S is the relative standard uncertainty due to subsampling.

The reference date and time for the measurement result is the time of the radium separation.

12.5 Calculate the critical activity concentration, x_C, as follows:

$$x_C = \frac{1.645\sqrt{\frac{C_B}{t_B}\left(\frac{1}{t_S}+\frac{1}{t_B}\right)+\xi_B^2}}{2.22\times V\varepsilon Y D} \quad (9)$$

where the other symbols are as defined above. To make a detection decision for the presence of ^{228}Ra in the sample, compare x to x_C.

12.6 Calculate the minimum detectable concentration (MDC) as follows:

$$x_D = \frac{\frac{3}{t_S}+3.29\sqrt{R_B\left(\frac{1}{t_S}+\frac{1}{t_B}\right)+\xi_B^2}}{2.22\times V\varepsilon Y D\times(1-1.645^2\varphi_S^2)} \quad (10)$$

where

x_D	is the minimum detectable concentration (pCi/L or pCi/g),
R_B	is the background count rate (cpm),
t_S	is the gross (sample) count time (min),
t_B	is the background count time (min),
ξ_B	is the non-Poisson uncertainty of the background correction (cpm),
ε	is the beta counting efficiency (cpm/dpm),
V	is the sample aliquant volume (L) or mass (g),
Y	is the chemical recovery or yield,
D	is the correction factor for ingrowth and decay of ^{228}Ac, and
φ_S	is the relative uncertainty due to subsampling.

Note: The MDC is properly used as a measure of the detection capability of the measurement process. It should never be used as a detection threshold.

12.7 Calculate the minimum quantifiable concentration (MQC).

$$x_Q = \frac{k^2\left(1+\sqrt{1+4(1-k^2\varphi^2)\frac{t_S^2}{k^2}\left(R_B\left(\frac{1}{t_S}+\frac{1}{t_B}\right)+\xi_B^2\right)}\right)}{2\times(2.22\,\text{dpm/pCi})\times(1-k^2\varphi^2)\times t_S\times V\times\varepsilon\times Y\times D}$$

where

x_Q	is the minimum quantifiable activity concentration
k	is 10
φ^2	is $u_r^2(V)+u_r^2(\varepsilon)+u_r^2(Y)+\varphi_S^2$
R_B	is the background count rate
t_S	is the sample gross count time (typically 100 min)
t_B	is the background count time (1000 min to 3000 min)
ξ_B	is the variability of background correction (nominally 0.05 min^{-1})
V	is the sample aliquant volume or mass
E	is the beta detection efficiency
Y	is the chemical yield (nominally 0.7)
D	is the product of ^{228}Ac ingrowth and decay factors

13.0 DATA REVIEW

13.1 The analyst reviews and control charts the chemical yield of the ^{228}Ra standard to determine acceptance of associated sample results. If the chemical yield of the standard is not within the three sigma control chart bounds, the associated sample results are unacceptable.

13.2 General Procedures.

13.2.1 See *NAREL Standard Operating Procedure for the Review of Radiochemistry Data* for general procedures for data review.

13.2.2 The proportional counting system administrator or another person designated by the Nuclear Counting Laboratory Manager performs the first official review of ^{228} Ra analysis results. However, the instrument operator should double-check his or her data entry for each analysis even if he or she is not the designated first reviewer.

14.0 METHOD PERFORMANCE

14.1 Between April 2007 and August 2011, NAREL participated in nine rounds of the Environmental Resource Associates (ERA) radiochemical proficiency-testing study for Ra-228 in water. The results are summarized below:

Date	Target Value (pCi/L)	NAREL Result	% Recovery
2007/4	18.2	18.9	104
2007/10	17.9	17.24	96
2008/4	17.0	13.62	80
2008/10	14.1	10.5	74
2009/4	13.6	12.48	92
2009/10	14.9	13.39	90
2010/4	15.1	15.38	102
2010/10	9.89	9.7	98
2011/4	11.6	10.5	91

The average value of % R is 91.9.

15.0 POLLUTION PREVENTION

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA places pollution prevention as the management option of first choice.

15.2 Volumes of prepared reagents are made in the smallest amounts consistent with sample batch sizes to minimize having to discard unused reagents.

16.0 WASTE MANAGEMENT

16.1 The EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. It is the responsibility of each laboratory to assure adherence to EPA regulations.

16.2 Waste streams generated by this procedure include the following: 2.0 mL of 18 M sulfuric acid, 90.0 mL of 0.17 M DTPA, 3.0 mL of 20 % sodium sulfate, 12.0 mL of 6M acetic acid, 20.0 mL of actinium wash (pH 3.0), 10.0 mL of 15 % HDEHP, and 10.0 mL of acetone. The waste is disposed of in accordance with the *NAREL Chemical Hygiene Plan*.

17.0 REFERENCES

17.1 Johnson, J.O., "Determination of Radium-228 in Natural Waters. Radiochemical Analysis of Water," Geological Survey Water–Supply Paper 1969-G., U.S. Government Printing Office, Washington, D.C. (1971).

17.2 Percival, D.R. and Martin, D.B., "Sequential Determination of Radium-226, Radium-228, Actinium-227, and Thorium Isotopes in Environmental and Process Waste Samples," Analytical Chemistry **46**: 1742–1749 (1974).

17.3 Krieger, H.L. and Whittaker, E.L., "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," EPA-600/4-80-032, Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio (1980).

17.4 Blanchard, R.L., Strong, A.B., Lieberman, R., and Porter, C.R., "The Eastern Environmental Radiation Facility's Participation in Interlaboratory Comparisons of Environmental Sample Analyses," Office of Radiation Programs, EPA, Technical Note, ORP/EERF-79-2 (1979).

17.5 Blanchard, R.L., Broadway, J.A., and Moore, J.B., "The Eastern Environmental Radiation Facility's Participation in Interlaboratory and Intralaboratory Comparisons of Environmental Sample Analyses: 1979–1980," U.S. Environmental Protection Agency Report, EPA 520/5-82-012 (1982).

17.6 Moore, J.B., Broadway, J.A., and Blanchard, R.L., "The Eastern Environmental Radiation Facility's Participation in Interlaboratory and Intralaboratory Comparisons of Environmental Sample Analyses: 1981–1986," U.S. Environmental Protection Agency Report, EPA 520/5-89-008 (1989).

17.7 Standard Methods for the examination of water and waste water 15th ed, American Public Health Association, Washington, D.C. (1980).

17.8 NAREL Radiochemistry Quality Assurance Manual (QA/QAM-1).

17.9 *NAREL Chemical Hygiene Plan*.

17.10 *NAREL Standard Operating Procedure for Preparing Solid Samples for Radium-226 and Radium-228 Analysis* (AMS/SOP-1)

17.11 *NAREL Standard Operating Procedure for Preparing Water Samples for Radium-226 and Radium-228 Analysis* (AMS/SOP-2)

18.0 APPENDICES (TABLES, DIAGRAMS, AND FLOWCHARTS)

18.1 Radium-228 Procedure Part 1

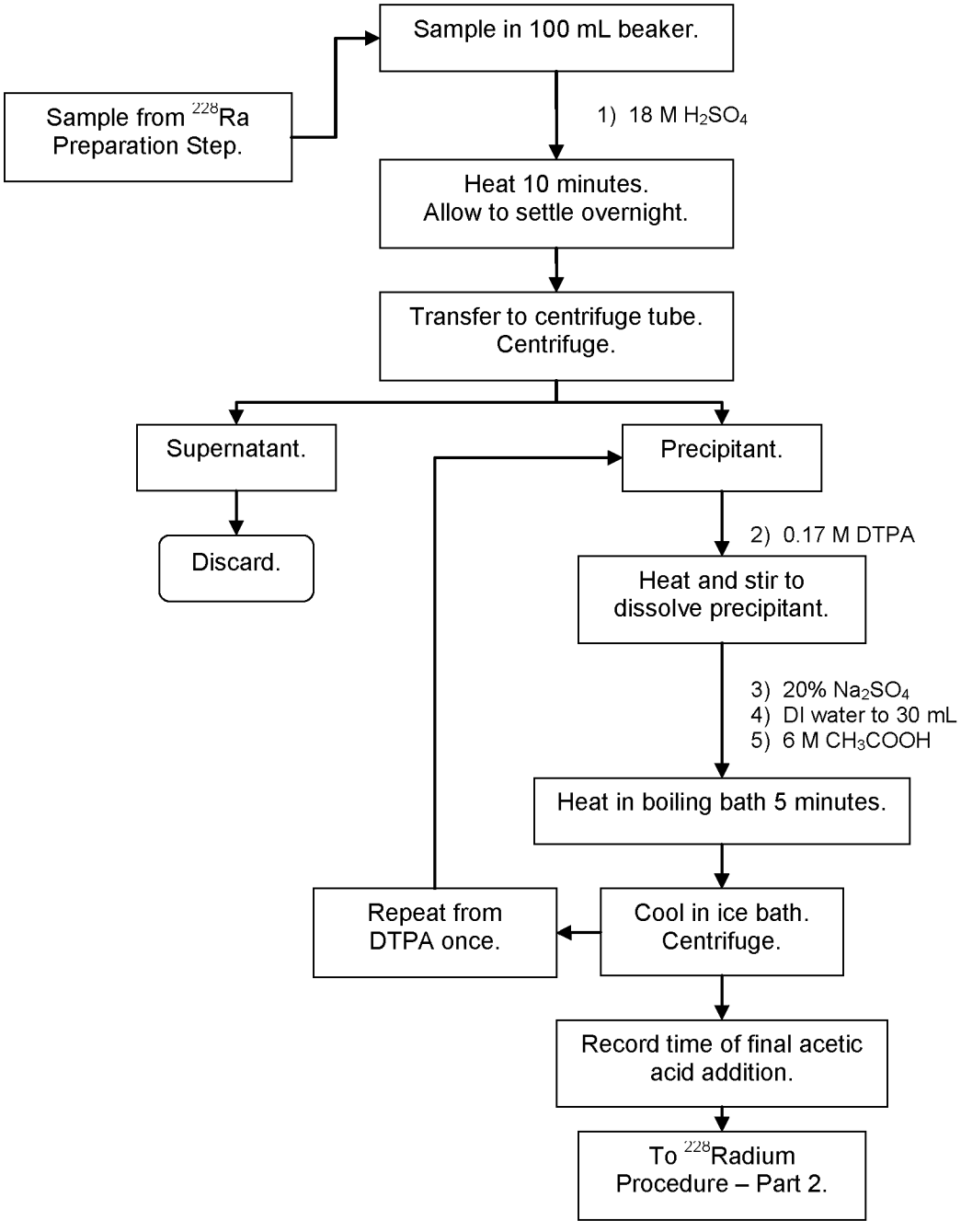
18.2 Radium-228 Procedure Part 2

18.3 Radium-228 Procedure Part 3

18.4 ^{228}Ra One-Point Calibration with Uncertainty

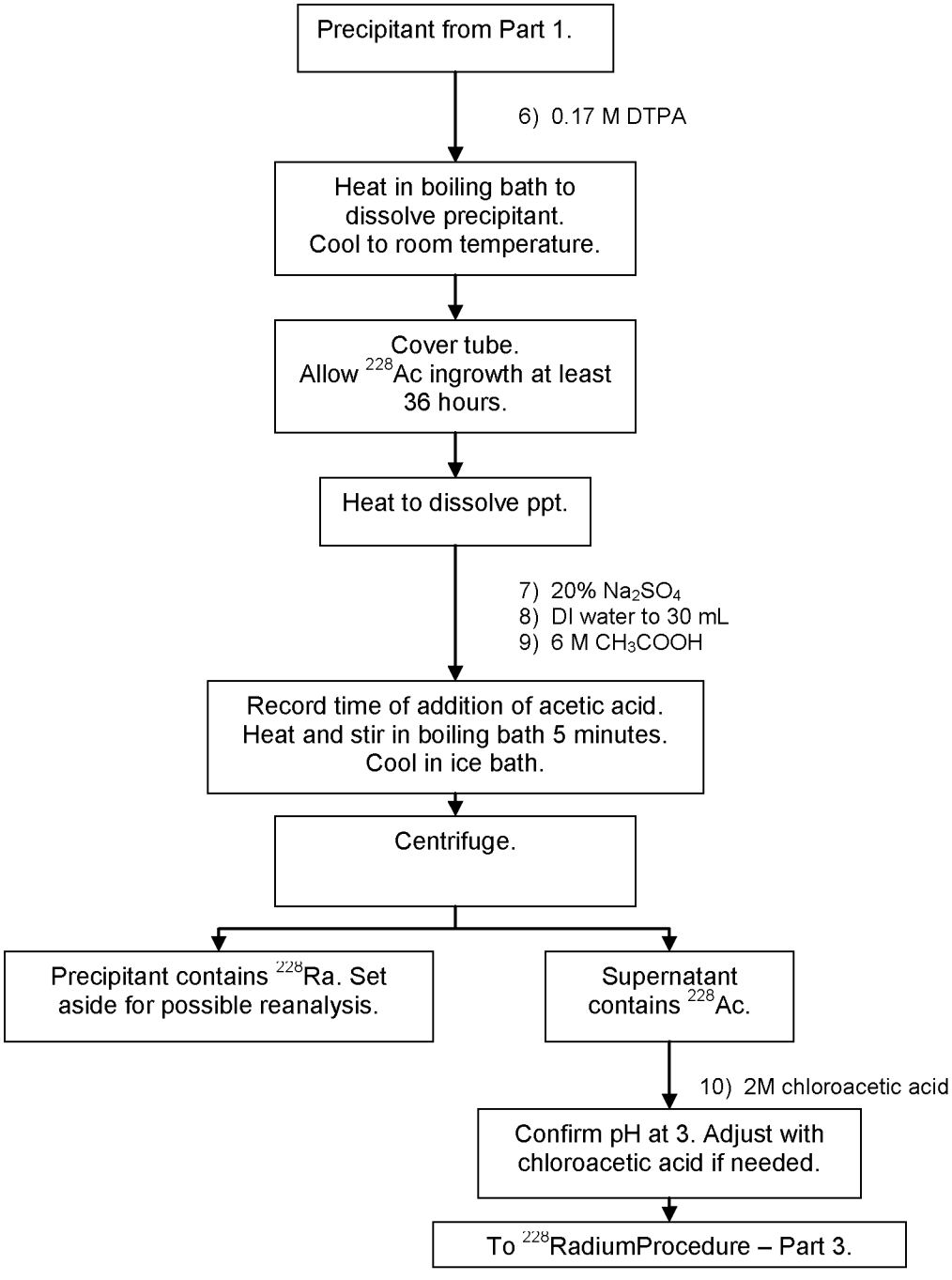
Appendix 18.1

Radium-228 Procedure – Part 1



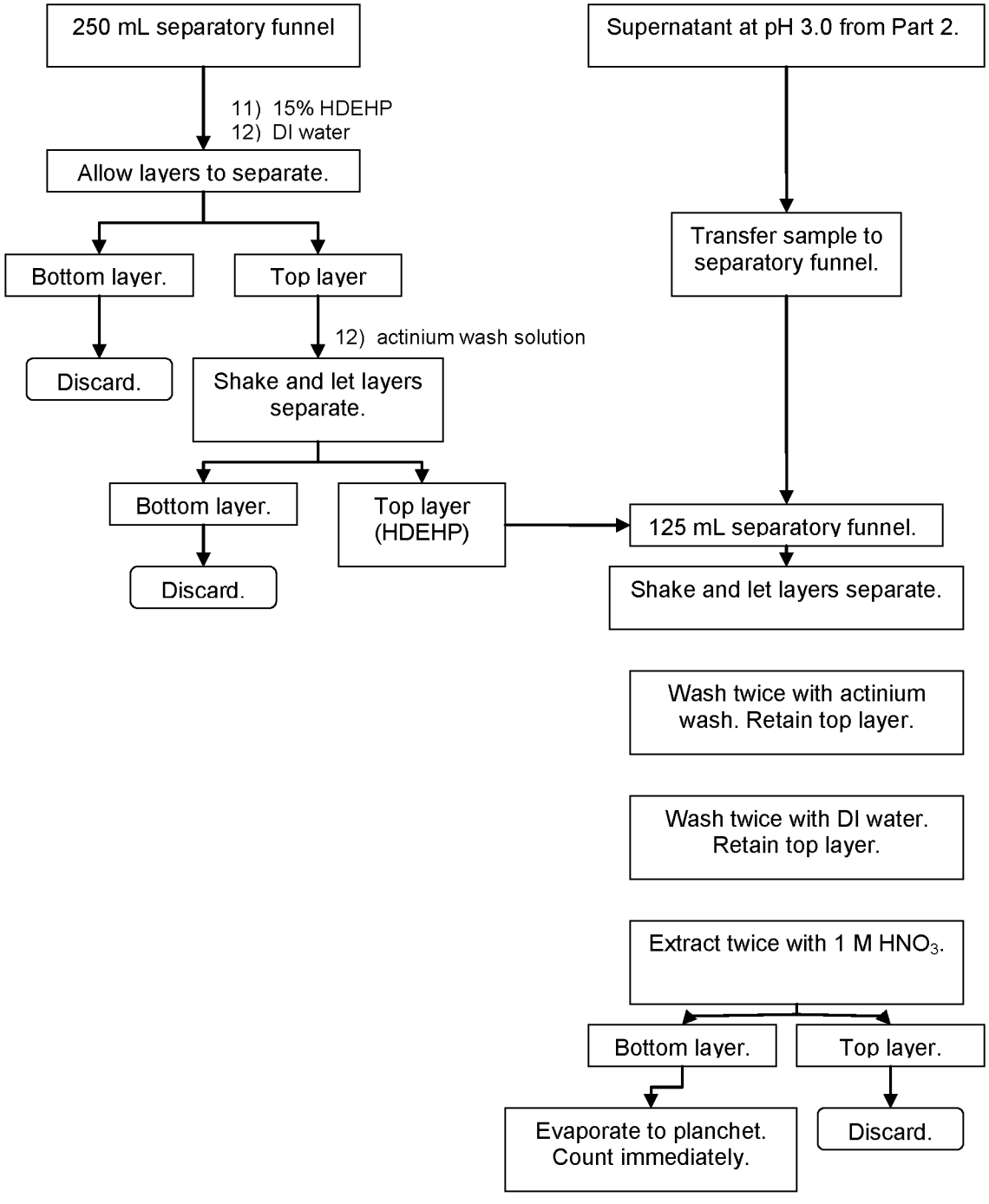
Appendix 18.2

Radium-228 Procedure – Part 2



Appendix 18.3

Radium-228 Procedure – Part 3



Appendix 17.4

^{228}Ra One-Point Calibration with Uncertainty

This appendix describes the procedure used to calculate detection efficiencies and their uncertainties during instrument calibration (at Step 8.10). The uncertainty estimates obtained here include components due to counting statistics, the calibration standard, and any additional variability observed in the pooled data set.

Procedure

Number the detectors being calibrated from 1 to n_{D}. Number the calibration sources used from 1 to n_{S}. For each detector d and each source s, calculate

$$R_{ds} = \frac{C_{\mathrm{S},ds}/t_{\mathrm{S},ds} - C_{\mathrm{B},ds}/t_{\mathrm{B},ds}}{V_{\mathrm{s}} \times DF_{ds}}$$

where

$C_{\mathrm{S},ds}$	is the gross count for the measurement of source s on detector d,
$C_{\mathrm{B},ds}$	is the background count for the same measurement
$t_{\mathrm{S},ds}$	is the count time for source s on detector d
$t_{\mathrm{B},ds}$	is the background count time for the measurement of source s on detector d
V_s	is the volume of the standard solution used in source s

and where DF_{ds} is the decay factor for the measurement, given by

$$DF_{ds} = \mathrm{e}^{-\lambda(t_{1,ds} - t_0)} \times \frac{1 - \mathrm{e}^{-\lambda t_{\mathrm{S},ds}}}{\lambda t_{\mathrm{S},ds}}$$

where

λ	is the decay constant for ^{89}Sr
t_0	is the reference date and time of the standard solution
$t_{1,ds}$	is the date and time at the start of the measurement of source s on detector d

Calculate an average value of R_{ds} for each detector d.

$$\widetilde{R}_d = \frac{1}{n_{\mathrm{S}}} \sum_{s=1}^{n_{\mathrm{S}}} R_{ds}$$

Alternatively, calculate $\widetilde{R}_d$ as a weighted average

$$\widetilde{R}_d = \sum_{s=1}^{n_{\mathrm{S}}} \frac{R_{ds}}{u_{\mathrm{P}}^2(R_{ds})} \Big/ \sum_{s=1}^{n_{\mathrm{S}}} \frac{1}{u_{\mathrm{P}}^2(R_{ds})}$$

where

$$u_{\mathrm{P}}^2(R_{ds}) = \frac{C_{\mathrm{S},ds}/t_{\mathrm{S}}^2 + C_{\mathrm{B},ds}/t_{\mathrm{B}}^2}{V_s^2 \times DF_{ds}^2}$$

Now estimate the "excess" relative standard uncertainty ξ due to random effects other than counting statistics. Given a non-negative value ξ for this excess relative uncertainty, for each detector d, a new weighted average $\hat{R}_d$ and an associated chi-squared statistic χ_d^2 can be calculated, as shown below.

$$u_{\mathrm{P}}^2(R_{ds}) = \frac{\widetilde{R}_d}{t_{\mathrm{S},ds} \times V_s \times DF_{ds}} + \frac{\dfrac{C_{\mathrm{B},ds}}{t_{\mathrm{B},ds}}\left(\dfrac{1}{t_{\mathrm{S},ds}} + \dfrac{1}{t_{\mathrm{B},ds}}\right)}{V_s^2 \times DF_{ds}^2}$$

$$\hat{R}_d = \sum_{s=1}^{n_{\mathrm{S}}} \frac{R_{ds}}{u_{\mathrm{P}}^2(R_{ds}) + \xi^2 \widetilde{R}_d^2} \Big/ \sum_{s=1}^{n_{\mathrm{S}}} \frac{1}{u_{\mathrm{P}}^2(R_{ds}) + \xi^2 \widetilde{R}_d^2}$$

$$u(\hat{R}_d) = \sqrt{\left(\sum_{s=1}^{n_{\mathrm{S}}} \frac{1}{u_{\mathrm{P}}^2(R_{ds}) + \xi^2 \widetilde{R}_d^2} \right)^{-1}}$$

$$\chi_d^2 = \sum_{s=1}^{n_{\mathrm{S}}} \frac{(R_{ds} - \hat{R}_d)^2}{u_{\mathrm{P}}^2(R_{ds}) + \xi^2 \widetilde{R}_d^2}$$

To estimate the actual value of ξ, use bisection (an iterative algorithm) to find the value of ξ that makes

$$\sum_{d=1}^{n_{\mathrm{D}}} \chi_d^2 = n_{\mathrm{D}}(n_{\mathrm{S}} - 1)$$

The initial range of possible values for ξ can be assumed to be $[0,1]$. Note that smaller values of ξ increase the sum on the left, while larger values decrease it. If it happens that

$$\sum_{d=1}^{n_{\mathrm{D}}} \chi_d^2 < n_{\mathrm{D}}(n_{\mathrm{S}} - 1)$$

even when $\xi = 0$, then set $\xi = 0$. Take the corresponding value of $\hat{R}_d$ and its uncertainty $u(\hat{R}_d)$, and use them to calculate the detection efficiency for detector d and its uncertainty.

$$\varepsilon_d = \frac{\hat{R}_d}{c_{\mathrm{S}}} \quad \text{and} \quad u(\varepsilon_d) = \sqrt{\frac{u^2(\hat{R}_d)}{c_{\mathrm{S}}^2} + \varepsilon_d^2 \frac{u^2(c_{\mathrm{S}})}{c_{\mathrm{S}}^2}}$$

where c_{S} denotes the activity concentration of the standard solution used for calibration.

Print the final estimate of the excess relative uncertainty ξ. Values smaller than 1 % are best. Values larger than 2 % indicate the possibility of spurious errors in the data, and warrant investigation.

For each detector d print the final value of χ_d^2 and print the corresponding “P-value” based on a chi-squared distribution with $n_{\mathrm{S}} - 1$ degrees of freedom. The P-value is calculated by the equation

$$p = 1 - P\left(\frac{n_{\mathrm{S}} - 1}{2}, \frac{\chi_d^2}{2}\right)$$

where P denotes the incomplete gamma function. A small P-value (e.g., smaller than 1 %) for a detector suggests a spurious error and should be investigated.